

"Separation of Solids in the Surface-layers of Solutions and 'Suspensions' (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation). — Preliminary Account." By W. RAMSDEN, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. GORCH, F.R.S. Received June 8,—Read June 18, 1903.

In a paper published in Du Bois Reymond's '*Archiv für Anat. und Physiologie*' in 1894,\* I showed that mere agitation of various proteid solutions brought about a separation of some of their contained proteid in the form of fibrous or membrano-fibrous solids, and that it was possible in this way to coagulate and remove the whole of the proteid from solutions of egg-albumin. It was proved also that these de-solutions and coagulations of proteid were not due to the action of enzymes, heat, or surface evaporation, and were not appreciably affected by the nature of the gas in contact with the liquid or of the vessel in which the agitation was effected.

A prolonged series of further experiments, undertaken with a view of ascertaining the precise cause of this phenomenon, has led me to the discovery of an important, but hitherto unnoticed physical fact:—namely, that, quite apart from evaporation, solid or highly viscous coatings are spontaneously, and more or less rapidly formed on the free surfaces of all proteid solutions.

By purely mechanical means these free-surface coatings can be heaped up to form visible solid masses of proteid, which in some cases is not only "de-soluted," but at the same time coagulated and rendered permanently insoluble in the mother-liquid.

By extending the range of my experiments, I have been led to the further conclusion that similar coatings of solid or highly viscous matter occur on the free surfaces of a large number of non-proteid colloid solutions, of fine and coarse "suspensions," and of a few apparently crystalloid solutions, and that they are formed also at the interfaces of every pair of liquids which, without being of high viscosity, are capable of forming persistent emulsions.

The explanation of these spontaneous de-solutions of previously dissolved matter at the free surfaces must be sought in the observation, which I have found to hold good in all cases hitherto examined, that the matter which accumulates possesses the property of lowering the surface-tension, and, therefore, the "surface energy," of the free surface of water.

On dynamical grounds, the most stable arrangement of any solution,

\* "*Physiologische Abtheilung*," pp. 517—534.

taking surface-tension considerations only into account, must be one accompanied by minimal "surface energy." A dissolved substance, if it increases the potential energy of a surface, will tend to leave that surface, or if it diminishes it, to accumulate at that surface. This principle has been recognised as holding good in crystalloid solutions\* but has not hitherto been shown to apply to colloid solutions and coarse "suspensions."

The same considerations may be applied in explanation of the accumulations observed at the interfaces of liquids forming persistent emulsions.

The formation of surface pellicles, the separation of various solids by mechanical treatment adapted to produce heaping up of surface-films, the power of forming moderately persistent bubbles possessed by various limpid solutions, and the power of forming persistent emulsions possessed by various immiscible liquids, are all explained (in the numerous cases where there is no evidence of chemical change) as due to diminution of the surface-energy brought about by accumulation of certain dissolved or suspended matters at the surfaces concerned, and to the physical properties of the accumulated material.

It is remarkable that the very common occurrence of these free-surface accumulations has hitherto escaped general notice. Doubtless this is due to the extreme delicacy and fragility of the solid coating, and to its generally rapid re-solution when by contraction of the surface it is heaped up in local excess, or when by the substitution of some other surface, the reason for such accumulation has been removed. For the production of *visible* masses of solid, or of deformed angular bubbles, it is in fact necessary that the surface-solid shall either be rendered insoluble by the mechanical treatment to which it is subjected, or shall be heaped up more rapidly than it is re-dissolved.

Full details of the methods employed, the control experiments made, and the results obtained, together with references to the work of others in the same field, I hope to publish shortly. Meanwhile a brief summary of the main points will be found in the following observations :—

1. The presence of a free (*i.e.*, gas) surface is essential for the production of the de-solutions and coagulations described in my previous paper.

2. By simple and gentle mechanical means adapted to produce heaping up of the surface-films, large masses of solid ("mechanical surface aggregates") can be separated out from all proteid solutions and from a large number of colloid solutions and suspensions. (*Vide* table at end of paper.) In the three cases where the dilution-limit has been ascertained, solid "mechanical surface aggregates" have been

\* *Vide* J. J. Thomson, "Application of Dynamics to Physics and Chemistry," p. 251.

obtained from liquids containing as little as one part of dissolved or suspended solid in 1,000,000 parts of water.

3. The separated solids differ greatly from one another in the rapidity and completeness of their re-solubility in the mother liquid, and they are sometimes insoluble and "coagulated."

4. They may have a delicate membranous, membrano-fibrous, or fibrous structure, simulating that of various biological tissues, or they may consist of particles lying loosely side by side (*e.g.*, sulphur).

5. The film of the free surface of all proteid solutions, and many of the various solutions or suspensions which yield solid "mechanical surface aggregates," exhibits a specially high viscosity not met with in the bulk of the solution. This "special superficial viscosity" develops at very different rates in different solutions, and attains very different degrees of maximal intensity. In some solutions (*e.g.*, egg-albumin, saponin) it develops with great rapidity; in others (*e.g.*, serum-albumin, methyl-orange, ferric acetate, mastic, etc.) several minutes or even hours may be necessary for any considerable development. Evaporation hastens its development, but is not essential. Slight convection currents have a powerful accelerating influence, but are essential only when the suspended solid is indiffusible. The nature of the gas in contact with the "solution" is a matter of indifference, provided it be chemically inactive.

6. In most cases the "special superficial viscosity" is accompanied by a special superficial resistance to "shear." This is often so intense that a magnetised needle floating on the solution is capable of rotating the vessel containing the solution, if this be floated on water or suspended by a fine thread and the needle be exposed to the attraction of a magnet.

7. The presence on a liquid of a thin coating of matter (even of liquid) which diminishes the "surface energy" would account for some "special superficial viscosity" (Marangoni), but would not account for superficial resistance to "shear," unless the coating of matter were solid or highly viscous and also coherent.

8. Bubbles of solutions of egg-albumin, caseinogen and saponin exhibit remarkable phenomena, which show that the bubble-film as a whole is very imperfectly elastic and is covered with solid membranes. Egg-albumin bubbles are deformed on collapse by the formation of persistent folds of solid proteid in the bubble-film. Bubbles of pure saponin solution, containing 0.01 per cent. or more of saponin, fall on collapse into innumerable shimmering folds containing isolated curved rods of *solid* saponin, although water is capable of dissolving at least 2500 times this amount.

The collapsing bubble assumes extraordinary shapes, with sharp angles (as observed by Plateau), and when a hanging bubble is broken, a *ragged* curtain of bubble-film, which instantly becomes dull and

opalescent, hangs for some 5 or 10 seconds from the edge of the supporting tube.

9. The presence of such solid membranes on a bubble must contribute greatly to its persistence. Further, the mere presence of solid particles on the surfaces of a bubble has, in many cases, been found to add greatly to its persistence, even when, judging by the absence of a special resistance to shear in the film of a free surface of the solution, such particles are not appreciably coherent, but lie loosely side by side (*e.g.*, in suspensions of sulphur, picric acid, quinine bisulphate, salicylic acid).

In the cases quoted, a bubble of air can be seen to pick up the particles in suspension as it passes through the liquid, and to retain them obstinately when it reaches the surface and comes to rest, so that the bubble becomes thickly coated with solid particles, although the liquid contained only a small quantity of suspended solid, and this solid is specifically heavier than the solution.

10. Every solution capable of forming moderately persistent bubbles which has hitherto been examined has yielded solid or highly viscous mechanical surface aggregates. This very remarkable fact indicates that the power of forming such bubbles is due to the presence of matter which has accumulated at the free surfaces in a solid or highly viscous condition. The cohesion of the matter, so as to form an appreciably coherent membrane, is apparently not essential, but it occurs in most cases where the bubble is very persistent.

Plateau recognised this association of the power of forming persistent bubbles with a special superficial viscosity and a diminished surface-tension, but did not connect these phenomena with the formation of a coating of matter derived from the solution and specially concentrated at a free surface.\*

On theoretical grounds the presence of a thin film of liquid, even of low viscosity, on the free surfaces, should also be capable of increasing the persistence of a bubble if the liquid be such as diminishes the surface energy of the mother solution, but increased persistence brought about in this way appears to be very slight compared with that occurring when the coating consists of solid or highly viscous particles.

11. The effects which the presence of solid particles in the surface layer exercises upon the persistence, size and other properties of bubbles, depend on many factors. Many solutions in which surface accumulation of solid undoubtedly takes place have been found incapable of forming large or persistent bubbles. The size of the particles, their surface-tension relations, the rate of their accumulation, the rate of their re-solution when forced by mechanical means into local excess, and the elasticities and flexibility of any membrane

\* *Vide* 'Statique des Liquides,' pp. 69—71.

formed, are all concerned in conferring on different bubbles the marked individuality which characterises them, and in making the formation of large or persistent bubbles possible. Solid particles, which diminish the surface energy of the free surface, may be regarded as adding in three ways to the persistence of a bubble:—

- i. By serving as *points d'appui*.\*
- ii. By actual contact, friction, or cohesion of the particles, opposing local disturbances of the film.
- iii. By opposing such deformation of the surface as tends to expose a new surface with higher surface-tension (*i.e.*, like oil on water, by the effect of the surface coating in diminishing the superficial energy).

12. It has been demonstrated that an actual solid membrane forms around the globules of several persistent emulsions, and at the contact interfaces of several pairs of liquids capable of forming persistent emulsions (*e.g.*, pure neutral olive oil and saponin solutions).

The membrane manifests itself by producing the following phenomena:—

- i. Intense viscosity peculiar to the interface, absent at the interface of pure water and the other liquid, and developing only when an emulsifying substance is added to one or other of the liquids.
- ii. Persistently deformed sharply angular and grotesque shapes of the emulsified globules.
- iii. Folds of semi-opaque membrane when the surface of separation is subjected to appropriate deformation.

Such direct optical evidence of the presence of a constraining membrane separating liquids which form persistent emulsions is exceptional or, if it occur, is usually fugitive. (*Cf.* air-bubbles.) An intense "special interface viscosity," pointing to the presence of solid or highly viscous matter, has, however, been found with every pair of liquids capable of forming persistent emulsions hitherto examined.

13. The persistence of many emulsions is therefore determined largely, among other factors, by the presence of solid or highly viscous matter at the interfaces of the two liquids. Direct measurements of the various surface tensions concerned are not available, but the close resemblance of the phenomena to those occurring at a free surface points to the view that accumulation of solid matter at the interfaces of the above emulsion-pairs occurs because the "surface-energy" is thereby diminished.

14. Numerous precipitations of colloids from their solutions by chloroform, ether, carbon bisulphide and amyl-alcohol, are attended by

\* *Cf.* Frankenheim, 'Die Lehre von der Cohäsion': Breslau, 1835.

precisely similar phenomena at the interfaces of the liquids concerned, and appear to be brought about in exactly the same way.

15. The suggestion that the observed surface accumulations must be attributed to the diminution of the "superficial energy" thereby produced is strongly supported by a series of experiments made with watery solutions containing equal quantities of two substances each of which by itself forms "mechanical surface aggregates." In such mixtures there has invariably been preferential accumulation of one substance to the more or less complete exclusion of the other from the mechanical surface aggregate obtained. Thus—

Saponin	> Egg-albumin.
Bile-salts	> Saponin.
"	> Soap.
"	> Gamboge.
"	> Egg-albumin.
"	> Sulphur.
Egg-albumin	> Carmine.

If the dissolved substances thus mixed exert no chemical action upon each other, such preferential accumulation is not only explicable, but, taking only surface-tension considerations into account, is theoretically essential when one substance produces a greater diminution of the surface energy than the other. In actual practice, however, the phenomena are complicated by differences in diffusibility and rate of re-solution and by limitation of independent mobility of the "dissolved" particles due to their mutual cohesions and adhesions.

16. It has been found also that bubbles blown from mixed solutions of two substances, each of which by itself forms bubbles presenting recognisable and well-marked differences of character, behave precisely as if they had been blown from a solution of one of these substances only, and this is always the one which in a mechanical surface aggregate made from the mixed solution is found to have more or less completely excluded the other, *e.g.* :—

Saponin	> Egg-albumin.
Bile-salts	> Saponin.
"	> Egg-albumin.
Egg-albumin	> Carmine.

17. The fact that the introduction of alcohol (and of other liquids of low surface-tension) into many solutions which show the above described surface phenomena frequently deprives those solutions of their superficial viscosity and of their power of forming bubbles or of yielding mechanical surface aggregates, would seem to be explicable by similar considerations, *i.e.*, as due to preferential

accumulation of alcohol to the exclusion of the suspended or dissolved solid.

18. Various hitherto obscure phenomena find their explanation in the facts observed, *e.g.* :—

- i. The ready formation of a “skin” on hot milk exposed to evaporation is explained by (a) The presence of a delicate skin or pellicle on the free surface even of cold milk or of caseinogen solutions not exposed to evaporation; (b) The presence of a similar pellicle at the inter-faces between caseinogen solutions and pure neutral olive oil or butter fat.

The existence of a proteid “haptogen-membrane” around the cream-globules of milk cannot any longer be doubted, and their rôle in contributing to the ready formation of a thick skin on hot milk, as first demonstrated by Hertz and Jamison,\* finds a complete explanation. The apparently contradictory observations of Rettger,† demonstrating the possibility of obtaining very delicate skins by heating caseinogen and other solutions, although free from fat globules, appear to be due to the dehydration and thickening by evaporation of the surface pellicles present on such solutions even in the cold.

- ii. The homogeneous “Grenz-membran” described by Bütschli (and the optical homogeneity of thin films referred to by Hardy) in various coagulated or dehydrated colloids, is the above-described membrane of solid colloid formed at an air or other appropriate surface.
- iii. The high pressure required to force solutions of saponin and albumin through capillary tubes when bubbles of air are present is largely due, among other factors, to the presence of solid membranes around the air-bubbles, and the increased resistance to deformation thus brought about. As Plateau showed, the resistance offered is enormously greater than that of water containing similar air bubbles. (Cf. air-embolism in the blood-capillaries of a mammal.)
- iv. The failure of proteids and other colloids in solution to pass through fine filters without considerable loss is largely due to the formation of surface membranes and mechanical coagula upon air, grease, or other suitable surfaces in the pores of the filter.

19. The following table indicates some of the substances whose aqueous solutions or suspensions have shown evidence of the accumulation of solid or highly viscous matter on their free surfaces, either by

\* *Vide* ‘Journ. of Physiol.’ London, 1901, vol. 27, p. 26.

† *Vide* ‘Amer. Journ. of Physiol.’ May, 1902.

Aqueous solutions or "suspensions" of—	Solid mechanical surface aggregates.	Intense superficial viscosity.	Persistent bubbles.
<b>Proteids of egg-white—</b>			
1 in 10 to 1 in 100,000.....	+	+	+
1 in 1,000,000.....	+	—	—
1 in 10,000,000.....	—	—	—
Crystalline egg-albumin.....	+	+	+
Serum proteids.....	+	+	+
Serum-albumin.....	+	+	+
Fibrinogen.....	+	+	+
Alkali-albumin.....	+	+	+
Acid albumin.....	+	+	+
Caseinogen in clear solution in Na <sub>2</sub> CO <sub>3</sub> solution.....	+	+	+
Gelatine.....	+	+	+
Primary albumose.....	+	+	+
Secondary albumose.....	+	+	+
Peptone (from peptic digestions) soluble in absolute alcohol.....	+	+	+
Muscle-proteids.....	+	+	+
Plant-vitellin from lentil seeds.....	+	+	+
Sodium palmitate.....	+	+	+
Sodium oleate.....	+	+	+
Methyl-orange.....	+	+	+
Orange G.....	+	+	+
Spiller's purple.....	+	+	+
Saponin, 1 in 100 to 1 in 100,000....	+	+	+
Saponin, 1 in 1,000,000..	+	+	—
Saponin, 1 in 10,000,000.....	—	—	—
Sapogenin.....	+	+	+
Digitalin.....	+	—	+
Ferric acetate.....	+	+	+
Cupric acetate.....	+	+	+
Colloidal ferric hydrate.....	+	+	+
Carmin.....	+	—	+
Colloidal sulphur.....	+	—	+
Bile-resin (dystysin).....	+	+	+
Bile salts.....	Viscous gum	—	+
"Caramel".....	+	+	+
Gum mastic.....	+	+	+
Shellac.....	+	+	+
Starch mucilage ( $\frac{1}{4}$ per cent.).....	+	—	—
Gamboge, 1 in 1,000.....	+	—	+
Gamboge, 1 in 1,000,000.....	+	—	—
"Flowers of sulphur".....	+	—	+
Animal charcoal.....	+	—	+
Quinine bisulphate (solution).....	—	—	—
Quinine bisulphate (excess in suspen- sion).....	+	—	+
Quinine solution.....	+	—	+
Picric acid (solution).....	—	—	—
Picric acid (excess in suspension)....	+	—	+
Salicylic acid (solution).....	—	—	—
Salicylic acid (excess in suspension)...	+	—	+



(1) yielding "mechanical surface aggregates;" (2) intense special superficial viscosity; or (3) forming persistent bubbles.

It will be seen that there is a very considerable parallelism in the three phenomena. Exact parallelism could not be expected, since the different physical properties of the surface accumulations must necessarily affect the phenomena in different and highly complex ways. Special superficial viscosity has only been recorded when very intense, and all minor degrees have been ignored, since the presence of dust, etc., in minute quantity may, as has been shown by Lord Rayleigh,\* produce some "superficial viscosity," and it has been practically impossible entirely to exclude such contamination. Power to form persistent bubbles has been shown by either :—

- i. The possibility of blowing 2-inch bubbles.
- ii. The formation of a froth.
- iii. The formation of small bubbles which last in closed vessels at least 30 minutes.

In all cases the substances employed have been of the greatest attainable purity, the de-soluted solids have been shown to consist of the same material as that in solution or suspension, and numerous control experiments have been made.

\* 'Roy. Soc. Proc.,' vol. 48, pp. 127—140, 1890.

---